

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2003-119398

(43)Date of publication of application : 23.04.2003

(51)Int.Cl.

C08L101/00
B29B 7/88
C08G 63/91
C08G 69/48
C08K 9/04
C08L 67/00
C08L 77/00

(21)Application number : 2001-312827

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(22)Date of filing : 10.10.2001

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(54) RESIN COMPOSITE MATERIAL AND METHOD FOR PRODUCING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a resin composite material which has excellent dynamic characteristics such as rigidity (strength, elastic modulus and the like), toughness and ductility, and excellent crystallization speed, and comprises at least two polymers and a laminar clay mineral, wherein different kinds of the polymers are sufficiently homogeneously compatibilized between the layers of the laminar clay mineral, and to provide a method for producing the same.

SOLUTION: This resin composite material is characterized by comprising a laminar clay mineral organized with the first and second organic onium salts, the first polymer bound to the laminar clay mineral through the first organic onium salt, and the second polymer bound to the laminar clay mineral through the second organic onium salt.

LEGAL STATUS

[Date of request for examination] 13.04.2004

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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CLAIMS

[Claim(s)]

[Claim 1] Resin composite material characterized by containing the stratified clay mineral made organic by the 1st and 2nd organic onium salt, the 1st polymer combined with said stratified clay mineral through said 1st organic onium salt, and the 2nd polymer combined with said stratified clay mineral through said 2nd organic onium salt.

[Claim 2] Resin composite material according to claim 1 characterized by for said 1st organic onium salt being organic onium salt which has a hydroxyl group, and for said 2nd organic onium salt being organic onium salt which has a carboxyl group, and being aliphatic series polyester which said 1st polymer combined with said stratified clay mineral through the hydroxyl group of said 1st organic onium salt, and being the aliphatic series polyamide which said 2nd polymer combined with said stratified clay mineral through the carboxyl group of said 2nd organic onium salt.

[Claim 3] Resin composite material according to claim 1 or 2 characterized by said 1st polymer being polylactic acid.

[Claim 4] Resin composite material given in any 1 term of the claims 1-3 characterized by the carbon number of said 1st and 2nd organic onium salt being six or more, respectively.

[Claim 5] A chemically-modified [which makes a stratified clay mineral organic by the 1st and 2nd organic onium salt / organic] degree, The 1st kneading process which melting kneading of the stratified clay mineral and the 1st polymer which are obtained to a chemically-modified [said / organic] degree is carried out [1st], and combines a stratified clay mineral and the 1st polymer through said 1st organic onium salt, The manufacture approach of the resin composite material which carries out melting kneading of the stratified clay mineral and the 2nd polymer which are obtained to a chemically-modified [said / organic] degree, and is characterized by including the 2nd kneading process which combines a stratified clay mineral and the 2nd polymer through said 2nd organic onium salt.

[Claim 6] A chemically-modified [which makes a stratified clay mineral organic by the 2nd organic onium salt which has the 1st organic onium salt and carboxyl group which has a hydroxyl group / organic] degree, The aliphatic series polyester kneading process of carrying out melting kneading of the stratified clay mineral and aliphatic series polyester which are obtained to a chemically-modified [said / organic] degree, and making the hydroxyl group of said 1st organic onium salt, and the end carboxyl group of said aliphatic series polyester reacting, Melting kneading of the stratified clay mineral and aliphatic series polyamide which are obtained to a chemically-modified [said / organic] degree is carried out. The manufacture approach of a resin composite material according to claim 5 characterized by including the aliphatic series polyamide kneading process of making the carboxyl group of said 2nd organic onium salt, and the end amino group of said aliphatic series poly polyamide reacting.

[Claim 7] the stratified clay mineral and the 1st polymerization nature compound which are obtained to a chemically-modified [which makes a stratified clay mineral organic by the 1st and 2nd organic onium salt / organic] degree, and a chemically-modified [said / organic] degree -- mixing -- this -- by the reaction of the 1st polymerization nature compound The 1st polymerization process which makes the 1st polymer combined with said stratified clay mineral through said 1st organic onium salt generate, The stratified clay mineral and the 2nd polymerization nature compound which are obtained to a chemically-modified [said / organic] degree are mixed. this -- the manufacture approach of the resin composite material characterized by including the 2nd polymerization process which makes the 2nd polymer combined with said stratified clay mineral through said 2nd organic onium salt by the reaction of the 2nd polymerization nature compound generate.

[Claim 8] A chemically-modified [which makes a stratified clay mineral organic by the 2nd organic onium salt which has the 1st organic onium salt and carboxyl group which has a hydroxyl group / organic] degree, The annular dimer and/or lactone of a stratified clay mineral and alpha-hydroxy acid which are obtained to a chemically-modified [said / organic] degree are mixed. The aliphatic series polyester polymerization process of making aliphatic series polyester generating by making the hydroxyl group of said 1st organic onium salt into a reacting point, The manufacture approach of a resin composite material according to claim 7 characterized by including the aliphatic series polyamide polymerization process of mixing the stratified clay mineral and lactams which are obtained to a chemically-modified [said / organic] degree, and making an aliphatic series polyamide generating by making the carboxyl group of said 2nd organic onium salt into a reacting point.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacture approach in detail about resin composite material and its manufacture approach at the resin composite material and the list containing at least two sorts of polymers, and a stratified clay mineral.

[0002]

[Description of the Prior Art] Conventionally, it is known that aliphatic series polyester, such as polylactic acid, shows the property decomposed by work of a microorganism and an enzyme and the so-called biodegradability. And the resin composite material which added the stratified clay mineral made organic by the organic-ized agent for the purpose of improvement in kinetic property, such as a biodegradation rate of aliphatic series polyester or rigidity, or the property of a crystallization rate to polylactic acid is proposed.

[0003] For example, the resin constituent which contains in JP,2000-17157,A and JP,2001-89646,A resin, such as aliphatic series polyester, and the stratified clay mineral made organic by organic-ized agents, such as an organic ammonium compound, is indicated.

[0004] Moreover, the sustained-release fertilizer which controlled the rate of dissolution of fertilizer using the coat ingredient containing lactic-acid system polyester and bloating tendency inorganic fillers, such as polylactic acid, is indicated by JP,2000-256087,A, and the stratified silicate by which swelling was carried out with 12-amino-dodecanoic-acid ammonium salt etc. is illustrated as a bloating tendency inorganic filler.

[0005]

[Problem(s) to be Solved by the Invention] However, even if it is the above-mentioned conventional resin composite material, it cannot necessarily be said that it is enough in respect of kinetic property, such as rigidity, toughness, and ductility, or a crystallization rate. Then, although the attempt which adds an aliphatic series polyamide etc. in order to raise the property of aliphatic series polyester is made, it is dramatically difficult for aliphatic series polyester and an aliphatic series polyamide to be hard to dissolve and to make homogeneity fully distribute these.

[0006] Moreover, although the approach of dehydration-polycondensation-compounding the block copolymer of polylactic acid and a polyamide by making this into a lactic acid is indicated by them after hydrolyzing epsilon caprolactam to Macromol.Chem.Phys., 199, and 2445 (1998), by the approach of starting, it is [that oligomer is only obtained and] and the resin with which practical use can be presented is not yet obtained.

[0007] this invention be make in view of the technical problem which the above-mentioned conventional technique have , and in the resin composite material containing at least two sorts of polymers , and a stratified clay mineral , polymers of a different kind be fully compatible in homogeneity between the layers of a stratified clay mineral , and it aim at provide a resin composite material excellent in kinetic property and crystallization rates , such as rigidity (reinforcement , elastic modulus , etc.) , toughness , and ductility , and a list with the manufacture approach .

[0008]

[Means for Solving the Problem] In order to solve the above-mentioned technical problem, resin composite material of this invention is characterized by containing the stratified clay mineral made organic by the 1st and 2nd organic onium salt, the 1st polymer combined with said stratified clay mineral through said 1st organic onium salt, and the 2nd polymer combined with said stratified clay mineral through said 2nd organic onium salt.

[0009] According to this invention, a stratified clay mineral is made organic by the 1st and 2nd organic onium salt. By combining this stratified clay mineral with the 2nd polymer through the 1st polymer and the 2nd organic onium salt through the 1st organic onium salt, respectively Even if it is the case that the compatibility between these polymers is essentially low, the polymers concerned can fully be dissolved in homogeneity between the layers of a stratified clay mineral. Consequently, resin composite material which has the property which was excellent in respect of mechanical properties, such as rigidity (reinforcement, elastic modulus, etc.), toughness, and ductility, or a crystallization rate is realized.

[0010] Moreover, the 1st manufacture approach of the resin composite material of this invention A chemically-modified [which makes a stratified clay mineral organic by the 1st and 2nd organic onium salt / organic] degree, The 1st kneading process which melting kneading of the stratified clay mineral and the 1st polymer which are obtained to a chemically-modified [said / organic] degree is carried out [1st], and combines a stratified clay mineral and the 1st polymer through said 1st organic onium salt, Melting kneading of the stratified clay mineral and the 2nd polymer which are obtained to a chemically-modified [said / organic] degree is carried out, and it is characterized by including the 2nd kneading process which combines a stratified clay mineral and the 2nd polymer through said 2nd organic onium salt.

[0011] Moreover, the 2nd manufacture approach of the resin composite material of this invention the stratified clay mineral and the 1st polymerization nature compound which are obtained to a chemically-modified [which makes a stratified clay mineral organic by the 1st and 2nd organic onium salt / organic] degree, and a chemically-modified [said / organic] degree -- mixing -- this -- by the reaction of the 1st polymerization nature compound The 1st polymerization process which makes the 1st polymer combined with said stratified clay mineral through said 1st organic onium salt generate, the stratified clay mineral and the 2nd polymerization nature compound which are obtained to a chemically-modified [said / organic] degree -- mixing -- this -- it is characterized by including the 2nd polymerization process which makes the 2nd polymer combined with said stratified clay mineral through said 2nd organic onium salt by the reaction of the 2nd polymerization nature compound generate.

[0012] While each of the 1st of this invention and 2nd manufacture approach makes association through the 1st organic onium salt form between the 1st polymer and a stratified clay mineral It is the thing which makes association through the 2nd organic onium salt form between the 2nd polymer and a stratified clay mineral. Since the 1st polymer and 2nd polymer can fully be dissolved in

homogeneity between the layers of a stratified clay mineral by this, the resin composite material of this invention excellent in kinetic property or a crystallization rate can be obtained efficiently and certainly.

[0013] In this invention, it is good also considering the 1st organic onium salt being organic onium salt which has a hydroxyl group, and the 2nd organic onium salt being organic onium salt which has a carboxyl group, and being aliphatic series polyester which the 1st polymer combined with the stratified clay mineral through the hydroxyl group of the 1st organic onium salt, and being the aliphatic series polyamide which the 2nd polymer combined with the stratified clay mineral through the carboxyl group of the 2nd organic onium salt as a description.

[0014] Moreover, a chemically-modified [to which the 1st manufacture approach of this invention makes a stratified clay mineral organic by the 1st and 2nd organic onium salt / organic] degree, The 1st kneading process which melting kneading of the stratified clay mineral and the 1st polymer which are obtained to a chemically-modified [said / organic] degree is carried out [1st], and combines a stratified clay mineral and the 1st polymer through said 1st organic onium salt, Melting kneading of the stratified clay mineral and the 2nd polymer which are obtained to a chemically-modified [said / organic] degree may be carried out, and the description of including the 2nd kneading process which combines a stratified clay mineral and the 2nd polymer through said 2nd organic onium salt may be carried out.

[0015] Moreover, a chemically-modified [to which the 2nd manufacture approach of this invention makes a stratified clay mineral organic by the 2nd organic onium salt which has the 1st organic onium salt and carboxyl group which has a hydroxyl group / organic] degree, The annular dimer and/or lactone of a stratified clay mineral and alpha-hydroxy acid which are obtained to a chemically-modified [said / organic] degree are mixed. The aliphatic series polyester polymerization process of making aliphatic series polyester generating by making the hydroxyl group of said 1st organic onium salt into a reacting point, It is good also considering including the aliphatic series polyamide polymerization process of mixing the stratified clay mineral and lactams which are obtained to a chemically-modified [said / organic] degree, and making an aliphatic series polyamide generating by making the carboxyl group of said 2nd organic onium salt into a reacting point as a description.

[0016] Thus, the stratified clay mineral made organic by the organic onium salt which has a hydroxyl group, and the organic onium salt which has a carboxyl group By making it combine with an aliphatic series polyamide through aliphatic series polyester and a carboxyl group through a hydroxyl group, respectively The low aliphatic series polyester and the aliphatic series polyamide of compatibility can fully be essentially dissolved in homogeneity between the layers of a stratified clay mineral, and resin composite material excellent in kinetic property and crystallization rates, such as rigidity, toughness, and ductility, is realized. In addition, since kinetic property and a crystallization rate can be further raised as the 1st polymer concerned is polylactic acid, it is desirable.

[0017] Moreover, in this invention, it is desirable that the carbon number of said 1st and 2nd organic onium salt is six or more, respectively. If a with a carbon numbers of six or more thing is used as 1st and 2nd organic onium salt, since the distance between layers of a stratified clay mineral will fully be spread by the organic onium salt concerned, the distributed homogeneity of the 1st and 2nd polymers and a stratified clay mineral is raised, and it is in the inclination whose kinetic property and crystallization rates, such as rigidity, toughness, and ductility, improve.

[0018]

[Embodiment of the Invention] Hereafter, the suitable operation gestalt of this invention is explained to a detail.

[0019] Resin composite material of this invention is characterized by containing the stratified clay mineral made organic by the 1st and 2nd organic onium salt, the 1st polymer combined with the stratified clay mineral through the 1st organic onium salt, and the 2nd polymer combined with the stratified clay mineral through the 2nd organic onium salt. Thereby, even if it is the case that the compatibility between the 1st and 2nd polymers is essentially low, the polymers concerned can fully be dissolved in homogeneity between the layers of a stratified clay mineral, and resin composite material which has the property which was excellent in respect of mechanical properties, such as rigidity (reinforcement, elastic modulus, etc.), toughness, and ductility, or a crystallization rate is realized.

[0020] Although not restricted especially as a stratified clay mineral concerning this invention, specifically, micas, such as vermiculite group; TENIO lights, such as kaolinite group; JIOKUTAHEDORARU vermiculites, such as smectite group; kaolinites, such as a montmorillonite, beidellite, saponite, and hectorite, and halloysite, and a trio KUTAHEDORARU vermiculite, a tetra-silicic mica, muscovite, an illite, a sericite, a FUROGO cutting tool, and biotite, etc. are mentioned. These stratified clay minerals may be natural minerals, and may be synthetic minerals by hydrothermal synthesis, scorification, a solid phase technique, etc. Moreover, in this invention, one sort in the above-mentioned stratified clay mineral may be used independently, and you may use combining two or more sorts. Moreover, as for the cation exchange capacity of a stratified clay mineral, it is desirable that they are 30-300meq / 100g.

[0021] Moreover, as the 1st and 2nd polymers used in this invention, although aliphatic series polyester, an aliphatic series polyamide, aromatic polyamide, a polycarbonate, polyimide, polyalkylene terephthalate, polyarylate, polyacetal, polyphenylene oxide, polyurethane, polyolefine, etc. are mentioned, when it uses combining aliphatic series polyester and an aliphatic series polyamide, since resin composite material which was more excellent in respect of kinetic property or crystal acceleration is realized, it is desirable.

[0022] Moreover, what the compound which functional groups, such as a hydroxyl group, a carboxyl group, an amino group, an isocyanate radical, an ester group, an epoxy group, and an acid-anhydride radical, combined with the organic radical in onium salt, such as organic ammonium salt, organic phosphonium salt, organic pyridinium salt, and organic sulfonium salt, as 1st and 2nd organic onium salt used in this invention is mentioned, and has the functional group which can form the polymer concerned and covalent bond according to the class of polymer mentioned above is selected suitably. For example, when using aliphatic series polyester and an aliphatic series polyamide as a polymer, by using the organic onium salt which has a hydroxyl group, aliphatic series polyester and a stratified clay mineral can be combined through the hydroxyl group of the organic onium salt concerned, and an aliphatic series polyamide and a stratified clay mineral can be combined through the carboxyl group of the organic onium salt concerned by using the organic onium salt which has another side and a carboxyl group.

[0023] As for the carbon number of the 1st and 2nd organic onium salt used by this invention, it is desirable respectively that it is six or more. Distance between layers of a stratified clay mineral cannot fully extend that the carbon number of the organic onium salt concerned is less than six, but it is in the inclination for the distributed homogeneity of a polymer and a stratified clay mineral to fall.

[0024] In addition, organic-ization as used in the field of this invention means adsorbing and/or combining the organic substance between the layers of a stratified clay mineral, and/or with a front face by the physical and chemical approach (preferably the chemical approach), and the distance between layers of a stratified clay mineral can fully be extended by organic-ization by the organic onium salt concerned. Moreover, although not restricted especially as a pair anion of this organic onium salt, halogen anions, such as Cl-, Br-, and I-, are used preferably, for example.

[0025] Moreover, in this invention, not all the 1st and 2nd polymers contained in resin composite material need to combine with the stratified clay mineral, and those parts should just join together.

[0026] Moreover, in the resin composite material of this invention, the 3rd polymer combinable with the 3rd organic onium salt and this may be contained further that at least two sorts in the above-mentioned polymer, and those polymers and at least two sorts of organic onium salt which can form covalent bond should just contain.

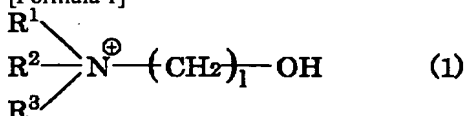
[0027] The resin composite material which the 2nd organic onium salt is organic onium salt which has a carboxyl group, the 1st organic onium salt is organic onium salt which has a hydroxyl group as an especially desirable operation gestalt of this invention, and is [is aliphatic series polyester which the 1st polymer combined with the stratified clay mineral through the hydroxyl group of the 1st organic onium salt, and] the aliphatic series polyamide which the 2nd polymer combined with the stratified clay mineral through the carboxyl group of the 2nd organic onium salt can be illustrated. Hereafter, this resin composite material is explained to a detail.

[0028] As for the content of the organic onium salt which has a hydroxyl group, it is desirable that it is the 10 - 150 weight section to the stratified clay mineral 100 weight section, and it is more desirable that it is the 20 - 100 weight section. Distance between layers of a stratified clay mineral cannot fully extend that the content of the organic onium salt concerned is said under lower limit, but it is in the inclination for the distributed homogeneity over aliphatic series polyester and an aliphatic series polyamide to fall, and in exceeding another side and said upper limit, it is in the inclination for the amount of the organic onium salt introduced by physical adsorption to increase, and for the physical properties of resin composite material to be spoiled (for example, plasticization).

[0029] Although it will not be restricted as organic onium salt which has the hydroxyl group preferably used by this invention especially if it has a hydroxyl group, as for the carbon number, it is desirable that it is six or more. Distance between layers of a stratified clay mineral cannot fully extend that the carbon number of the organic onium salt concerned is less than six, but it is in the inclination for the distributed homogeneity over aliphatic series polyester and an aliphatic series polyamide to fall. The organic ammonium salt which has a hydroxyl group and is expressed with the following general formula (1) or (2) as organic onium salt whose carbon number is six or more is illustrated. One sort may be independently used for such organic ammonium salt, and it may use both together.

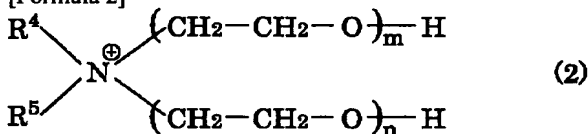
[0030]

[Formula 1]



[-- among the formula, even if R1, R2, and R3 are the same, you may differ, and a hydrogen atom or an alkyl group is expressed, respectively, and l expresses the integer of 6-20.]

[Formula 2]



[-- among the formula, even if R4 and R5 are the same, you may differ, a hydrogen atom or an alkyl group is expressed, respectively, even if m and n are the same, they may differ from each other, and the carbon number of the sum total of R4 and R5 is six or more, and they express the integer of 1-20.]

R1, R2, or R3 expresses a hydrogen atom or an alkyl group among the above-mentioned general formula (1). As this alkyl group, specifically A methyl group, an ethyl group, n-propyl group, i-propyl group, n-butyl, sec-butyl, tert-butyl, A straight chain or a branched-chain pentyl radical, a straight chain or a branched-chain hexyl group, a straight chain, or a branched-chain heptyl radical, A straight chain or a branched-chain octyl radical, a straight chain or a branched-chain nonyl radical, a straight chain, or a branched-chain decyl group, Although a straight chain or a branched-chain undecyl radical, a straight chain or the branched-chain dodecyl, a straight chain or a branched-chain tridecyl radical, a straight chain or a branched-chain tetradecyl radical, a straight chain or a branched-chain pentadecyl group, a straight chain, or a branched-chain octadecyl radical is mentioned As for the carbon number of the alkyl group concerned, it is desirable that it is 1-4. When the carbon number of an alkyl group exceeds said upper limit, it is in the inclination for composition of organic onium salt to become difficult.

[0031] moreover, the inside of the above-mentioned general formula (1) and l -- the polymerization degree of a methylene group (-CH2-) -- expressing -- 6-20 -- it is the integer of 8-18 preferably. When l is less than six, the distance between layers of a stratified clay mineral does not fully spread, but it is in the inclination for the distributed homogeneity over aliphatic series polyester and an aliphatic series polyamide to fall. On the other hand, when l exceeds 20, it is in the inclination for composition of organic onium salt to become difficult.

[0032] Moreover, R4 and R5 express a hydrogen atom or an alkyl group among the above-mentioned general formula (2). The alkyl group illustrated as this alkyl group in the explanation of R1, R2, and R3 in a general formula (1) is mentioned.

[0033] Although you may differ even if R4 and R5 in a general formula (2) are the same, as for the carbon number of those sum totals, it is desirable that it is six or more, and it is more desirable that it is eight or more. The distance between layers of a stratified clay mineral does not fully spread that the carbon number of the sum total of R4 and R5 is less than six, but it is in the inclination for the distributed homogeneity over aliphatic series polyester and an aliphatic series polyamide to fall. For example, R4 is preferably used as a compound with which the compound whose R5 is the compound whose R5 is the dodecyl in a hydrogen atom, and whose R4 is an octadecyl radical in a methyl group, and the compound R4 and whose R5 are octadecyl radicals fill the above-mentioned conditions.

[0034] moreover, the inside of the above-mentioned general formula (2), and m and n -- the polymerization degree of an oxyethylene radical (-CH2CH2O-) -- expressing -- 1-20 -- desirable -- 1-10 -- it is the integer of 1-5 more preferably, and is 1 especially preferably. When m or n exceeds 20, it is in the inclination for the hydrophilic property of a stratified clay mineral to become high superfluously, and for adjustment to become difficult. In addition, even if m and n are the same, they may differ.

[0035] Moreover, although it will not be restricted as organic onium salt which has a carboxyl group concerning this invention especially if it has a carboxyl group, as for the carbon number, it is desirable that it is six or more. Distance between layers of a stratified clay mineral cannot fully extend that the carbon number of the organic onium salt concerned is less than six, but it is in the inclination for the distributed homogeneity over aliphatic series polyester and an aliphatic series polyamide to fall. It has a carboxyl group and 8-amino octylic acid hydrochloride, a 12-amino-dodecanoic-acid hydrochloride, 18-amino octadecanoic acid hydrochloride, etc. are mentioned as a desirable example of the organic onium salt whose carbon number is six or more.

[0036] As for the content of the organic onium salt which has a carboxyl group, it is desirable that it is the 10 - 150 weight section to the stratified clay mineral 100 weight section, and it is more desirable that it is the 20 - 100 weight section. Distance between layers of a stratified clay mineral cannot fully extend that the content of the organic onium salt concerned is said under lower limit, but it is in the inclination for the distributed homogeneity over aliphatic series polyester and an aliphatic series polyamide to fall, and in exceeding another side and said upper limit, it is in the inclination for the amount of the organic onium salt introduced by physical adsorption to increase, and for the physical properties of resin composite material to be spoiled (for example, plasticization).

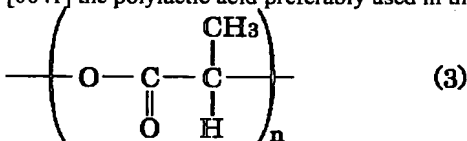
[0037] moreover -- although it is not restricted especially unless the compounding ratio of the organic onium salt which has a hydroxyl group, and the organic onium salt which has a carboxyl group spoils the property of resin composite material -- the compounding ratio concerned -- the mole ratio of a hydroxyl group and a carboxyl group -- desirable -- 1:99-99:1 -- more -- desirable -- 10:90-90:10 -- it is set up so that it may become within the limits of 20:80-80:20 still more preferably. It is in the inclination it to become difficult for the mole ratio of a hydroxyl group and a carboxyl group to dissolve aliphatic series polyester and an aliphatic series polyamide in homogeneity between the layers of a stratified clay mineral as the above is out of range.

[0038] Drawing 1 (a) - (c) is the explanatory view showing notionally the condition of the stratified clay mineral made organic by the two above-mentioned sorts of organic onium salt, respectively. In this invention, the both sides of organic onium salt 2a which has a hydroxyl group as shown in drawing 1 R> 1 (a), and organic onium salt 2b which has a carboxyl group may combine with the same layer of the stratified clay mineral 1, as shown in drawing 1 (b), two sorts of organic onium salt 2a and 2bs may combine with the separate layer of the stratified clay mineral 1, respectively, and these two joint gestalten may be intermingled further. Moreover, since each class which the stratified clay mineral 1 adjoins becomes possible [forming the stratified clay mineral which has a seemingly very large aspect ratio as having the shape of a flocculation (flocculation) which stood in a row near the edge] as shown in drawing 1 (c) when organic onium salt 2a and 2b combine with a separate layer, it is desirable.

[0039] The distance between layers of a stratified clay mineral can fully be extended, and aliphatic series polyester and an aliphatic series polyamide are introduced by these organic onium salt between layers. Here, as for the distance between layers of a stratified clay mineral, it is desirable that it is 5nm or more on the basis of the mean distance between the centers of gravity of each class, and it is more desirable that it is 10nm or more. It is in the inclination for distributed homogeneity [as opposed to / that the distance between layers of a stratified clay mineral is said under lower limit / aliphatic series polyester and an aliphatic series polyamide] to fall.

[0040] Moreover, as aliphatic series polyester concerning this invention, the ring-opening-polymerization object of lactone, such as an annular dimer of alpha-hydroxy acids, such as glycolide and a lactide (L-lactide, D-lactide, and a meso-lactide are included), and beta propiolactone, diketene, gamma-butyrolactone, delta-valerolactone, epsilon-KAPURARO lactone, may be mentioned, for example, and the polymers concerned may be any of a homopolymer and a copolymer. Moreover, the polylactic acid which is the ring-opening-polymerization object of a lactide also in the above-mentioned polymer is desirable. When polylactic acid is used, it is in the inclination whose kinetic property and crystallization rates, such as rigidity, toughness, and ductility, improve.

[0041] the polylactic acid preferably used in this invention -- following general formula (3): -- [Formula 3]



It is the polymer which has the repeat unit expressed with (n expresses an integer among a formula). Although especially the average molecular weight of the polylactic acid concerned is not restricted, it is desirable that it is 5,000-1,000,000. When it is in the inclination for the average molecular weight of polylactic acid to become insufficient [machine physical properties, such as reinforcement and an elastic modulus,] for it to be said under lower limit and said upper limit is exceeded, it is in the inclination for a fluidity to fall remarkably in the case of shaping.

[0042] In addition, although association through a hydroxyl group is formed between stratified clay minerals at the end of polylactic acid, the polymerization of glycolide, the caprolactone, etc. is further carried out to the other end, and it is good for it also as a copolymer. As for the polymerization chain of the polylactic acid in this copolymer, it is desirable that it is more than 80mol% on the basis of the whole copolymer.

[0043] Epsilon caprolactam, RAURO lactam, 2-azacyclo octanone, and 2-azacyclo nona non, moreover, as an aliphatic series polyamide concerning this invention, the ring-opening-polymerization object (nylon) of lactams, such as 2-azacyclo trideca non, may be mentioned, and the polymers concerned may be any of a homopolymer and a copolymer.

[0044] It is desirable that it is the 1 - 1000 weight section to the aliphatic series polyester 100 weight section, as for the loadings with an aliphatic series polyamide, it is more desirable that it is the 10 - 1000 weight section, and it is still more desirable that it is the 25 - 400 weight section. When the loadings of an aliphatic series polyamide are said under lower limit, it is in the inclination which becomes inadequate [the shock resistance or thermal resistance of resin composite material], and when another side and said upper limit are exceeded, it is in the inclination for an elastic modulus to fall.

[0045] Moreover, as for the loadings of a stratified clay mineral, it is desirable that it is 0.01 - 20 weight section to a total of 100 weight sections of the loadings of aliphatic series polyester and an aliphatic series polyamide, and it is more desirable that it is 1 - 12 weight section. When the loadings of a stratified clay mineral are in the inclination which becomes inadequate [extent of improvement in kinetic property, such as rigidity, or a crystallization rate by it being said under lower limit] and exceed another side and said upper limit, it is in the inclination which stiffens.

[0046] Next, the manufacture approach of the resin composite material of this invention is explained.

[0047] A chemically-modified [to which the 1st manufacture approach of this invention makes a stratified clay mineral organic by the 1st and 2nd organic onium salt / organic] degree, The 1st kneading process which melting kneading of the stratified clay mineral and the 1st polymer which are obtained to a chemically-modified [organic] degree is carried out [1st], and combines a stratified clay mineral and the 1st polymer through the 1st organic onium salt, Melting kneading of the stratified clay mineral and the 2nd polymer which are obtained to a chemically-modified [organic] degree is carried out, and it is characterized by including the 2nd kneading process which combines a stratified clay mineral and the 2nd polymer through the 2nd organic onium salt.

[0048] A chemically-modified [organic] degree can be performed by the approach currently indicated by for example, these people at the patent No. 2627194 official report. That is, organic-ization of a stratified clay mineral can be performed by carrying out the ion exchange of the inorganic ion in a stratified clay mineral by the organic onium ion (for example, setting to organic ammonium salt organic ammonium ion) produced from the 1st and 2nd organic onium salt.

[0049] When more specifically using the organic ammonium salt which has a hydroxyl group, and the organic ammonium salt which

has a carboxyl group, organic-ization can be performed by the following approaches. That is, when using a massive stratified clay mineral, first, a ball mill etc. grinds this and it is fine-particles-ized. Subsequently, these fine particles are underwater distributed using a mixer etc., and the water distribution object of a stratified clay mineral is obtained. Apart from this, acids, such as an organic amine which has a hydroxyl group, an organic amine which has a carboxyl group, and a hydrochloric acid, are added to water, and the water solution containing the two above-mentioned kinds of organic ammonium salt is prepared. By adding this water solution to the water distribution object of the above-mentioned stratified clay mineral, and mixing, the ion exchange of the inorganic ion in a stratified clay mineral is carried out by two kinds of organic ammonium ion produced from organic ammonium salt. By removing water from this mixture, the stratified clay mineral made organic with the organic ammonium salt which has a hydroxyl group, and the organic ammonium salt which has a carboxyl group is obtained.

[0050] As a dispersion-medium object of organic ammonium salt or a stratified clay mineral, the mixture of these and water can be used for a methanol, ethanol, propanol, isopropanol, ethylene glycol and such mixture, and a list besides water.

[0051] As described above to the chemically-modified [this / organic] degree, organic-ization by the 1st organic onium salt (organic onium salt which has a hydroxyl group), and the 2nd organic onium salt (organic onium salt which has a carboxyl group) may be performed simultaneously, and after making it organic by one organic onium salt, you may make it organic on the other hand.

[0052] Next, the resin composite material of this invention can be obtained by carrying out melting kneading of the stratified clay mineral and the 1st and 2nd polymers which are obtained to a chemically-modified [organic] degree. For example, when using the organic onium salt which has a hydroxyl group, the organic onium salt which has a carboxyl group, aliphatic-series polyester, and an aliphatic-series polyamide, association whose reaction of the carboxyl group of organic onium salt and the end amino group of an aliphatic-series polyamide which association which the hydroxyl group of organic onium salt and the end carboxyl group of aliphatic series polyester which have a hydroxyl group reacted, and minded the hydroxyl group among both is formed, and have a carboxyl group advanced, respectively, and minded the carboxyl group among both is formed. Thereby, aliphatic series polyester and an aliphatic series polyamide can fully be dissolved in homogeneity between the layers of a stratified clay mineral, and the resin composite material of this invention excellent in kinetic property and crystallization rates, such as rigidity, toughness, and ductility, can be obtained.

[0053] In the 1st manufacture approach In addition, kneading with the 1st polymer and a stratified clay mineral, After performing simultaneously kneading with the 2nd polymer and a stratified clay mineral and kneading one side of these polymers with a stratified clay mineral, the kneading object and another side which are obtained may be kneaded further (hereafter, although it is only called a "kneading process", the kneading process concerned includes the both sides of the above-mentioned procedure).

[0054] The temperature in a kneading process is suitably selected according to the class of reaction of a polymer and organic onium salt. For example, when performing the reaction of the carboxyl group of organic onium salt, and the end amino group of an aliphatic series polyamide in the reaction of the hydroxyl group of organic onium salt, and the end carboxyl group of aliphatic series polyester, and a list, the upper limit of the temperature concerned is 280 degrees C preferably, and is 250 degrees C more preferably. When the temperature concerned exceeds said upper limit, it is in the inclination for the molecular weight of aliphatic series polyester (or further aliphatic series polyamide) to fall, and for the physical properties of resin composite material to be spoiled (for example, plasticization). Moreover, although the lower limit of the temperature concerned changes with classes of aliphatic series polyester and aliphatic series polyamide, it is desirable that it is more than the melting point of a polymer with the low melting point among aliphatic series polyester or an aliphatic series polyamide. For example, since the melting point of polylactic acid is 170-180 degrees C, the melting point of nylon 6 is 225 degrees C and the melting point of Nylon 12 is 185 degrees C, when combining these, it is desirable to set up temperature more than the melting point of polylactic acid. If the conditions of the above [temperature] are not fulfilled, melting of aliphatic series polyester or an aliphatic series polyamide becomes inadequate, and it is in the inclination for such distributed homogeneity to fall.

[0055] Moreover, it is desirable to carry out according to the approach currently indicated by these people at the international disclosure WO 99/No. 50340 official report in the case of a kneading process. Namely, a 2 shaft kneading machine equipped with the screw which can add high resin reduced pressure, the quantity total amount of shear, and high shear energy is used. 5x104Pa or more and maximum 1x105Pa, [the average of resin reduced pressure] The total amount of shear can raise such distributed homogeneity more by carrying out melting kneading of the stratified clay mineral and the 1st and 2nd polymers which were made organic under the conditions 105-107, and whose total shear energy are 1010-1014Pa.

[0056] the stratified clay mineral and the 1st polymerization nature compound which are obtained to a chemically-modified [to which the 2nd manufacture approach of this invention makes a stratified clay mineral organic by the 1st and 2nd organic onium salt / organic] degree, and a chemically-modified [organic] degree -- mixing -- this -- by the reaction of the 1st polymerization nature compound The 1st polymerization process which makes the 1st polymer combined with the stratified clay mineral through the 1st organic onium salt generate, the stratified clay mineral and the 2nd polymerization nature compound which are obtained to a chemically-modified [organic] degree -- mixing -- this -- the 2nd polymerization process which makes the 2nd polymer combined with said stratified clay mineral through the 2nd organic onium salt by the reaction of the 2nd polymerization nature compound generate is included.

[0057] A chemically-modified [concerning the 2nd manufacture approach / organic] degree can be performed like a chemically-modified [concerning the manufacture approach of the above 1st / organic] degree.

[0058] Moreover, the 1st and 2nd polymerization processes may be performed simultaneously, and another side may be performed after performing one side of a polymerization process. For example, the following (i) - (iii) can be illustrated about the sequence of an aliphatic series polyester polymerization process and an aliphatic series polyamide polymerization process.

(i) After performing an aliphatic series polyester polymerization process, an aliphatic series polyamide polymerization process is performed.;

(ii) After performing an aliphatic series polyamide polymerization process, an aliphatic series polyester polymerization process is performed.;

(iii) The stratified clay mineral obtained to a chemically-modified [organic] degree, the annular dimer of alpha-hydroxy acid and/or lactone, and lactams are mixed, and an aliphatic series polyester polymerization process and an aliphatic series polyamide polymerization process are performed simultaneously.

[0059] Also in the above-mentioned procedure (i) - (iii), a procedure (i) is especially desirable. According to the procedure (i), such a phenomenon can fully be controlled and aliphatic series polyester with molecular weight large enough can be made to generate, although there is a possibility that the amide (polyamide generated by the lactam or its ring opening polymerization) generated in the case of a polymerization may serve as catalyst poison of a lactide polymerization, and may become inadequate [the molecular weight of aliphatic series polyester], in a procedure (ii) and (iii).

[0060] Moreover, the above-mentioned aliphatic series polyester polymerization process and an aliphatic series polyamide

polymerization process may be performed using a predetermined catalyst, and may be performed with a non-catalyst. As a catalyst, octylic acid-ized tin, tin chloride, a zinc chloride, a lead oxide, lead carbonate, a titanium chloride, alkoxy titanium, a germanium dioxide, a zirconium dioxide, etc. are mentioned, and, as for the amount used, specifically, it is desirable that it is 0.001 - 1 weight section to the polymerization nature monomer 100 weight section. Moreover, as for the reaction temperature in the polymerization process concerned, it is desirable that it is 100-200 degrees C.

[0061] Thus, while each of the 1st of this invention and 2nd manufacture approach makes association through the 1st organic onium salt form between the 1st polymer and a stratified clay mineral. It is the thing which makes association through the 2nd organic onium salt form between the 2nd polymer and a stratified clay mineral. Since the 1st polymer and 2nd polymer can fully be dissolved in homogeneity between the layers of a stratified clay mineral by this, the resin composite material of this invention excellent in kinetic property or a crystallization rate can be obtained efficiently and certainly.

[0062]

[Example] Hereafter, although this invention is explained still more concretely based on an example and the example of a comparison, this invention is not limited to the following examples at all.

[0063] 5000ml of 80-degree C water was made to distribute example 1 (organic-izing of stratified clay mineral) sodium mold montmorillonite (KUNIPAF made from KUNIMINE mining, cation-exchange-capacity: 115meq / 100g) 100g, and, on the other hand, dihydroxyethyl MECHIRUSUTEARIRU ammonium bromide (henceforth 18(OH)2) 36.4g, 7.4g (henceforth 12COOH) of 12-amino dodecanoic acid, and 3.3ml of concentrated hydrochloric acid were dissolved in 2000ml of 80-degree C water. Subsequently, the organic-ized montmorillonite which mixed both, and performed organic-ization of a montmorillonite and 18(OH)2 and 12COOH(s) added by the mole ratio of 7:3 was obtained. 80-degree C water washed the obtained organic-ized montmorillonite (henceforth 18(OH) 2-Mont) 3 times, and this was ground after freeze-drying. The residue for inorganic of the organic-ized montmorillonite for which it asked by the **** method was 64%.

[0064] (Kneading of polylactic acid and Nylon 12) Melting kneading of the mixture which added the above-mentioned organic-ized montmorillonite 4.3% of the weight with the inorganic part reduced property to polylactic resin (Shimadzu Lacty # 9030) was carried out using the twin screw extruder (Japan Steel Works TEX30alpha) equipped with a screw by screw-speed 300rpm, the resin temperature of 200 degrees C, and resin speed-of-supply 5 kg/h. As the weight ratio of polylactic acid and Nylon 12 was set to 7:3, it added Nylon 12 resin (Ube Industries nylon 3024B), melting kneading was performed further, and the target resin composite material was obtained from the middle of this kneading. After extruding the obtained resin composite material in the shape of a strand, it quenched with water and considered as the pellet with the strand cutter.

[0065] (Assessment of a distributed condition) The above-mentioned pellet was started with the microtome and the ultrathin section was produced. x: in which the stratified clay mineral in the condition that the **:2-3 layer to which this is observed with a transmission electron microscope (JEOL JOEL- 200 CX), and the following criteria: O:stratified clay minerals are carrying out micro-disperse of the distributed condition of a stratified clay mineral for every monolayer mostly condensed is accepted 50% or more -- most stratified clay minerals distribute, where dozens of or more layers are condensed -- **** -- it based and evaluated. The obtained result is shown in a table 1.

[0066] (Assessment of kinetic property) Injection molding of the above-mentioned resin composite material was performed using the injection molding machine (NISSEI PLASTIC INDUSTRIAL PS 40E2 ASE) and FS75 mold, and the dumbbell mold test piece for tensile test was obtained. This test piece is used and it is ASTM. The tensile test was performed according to D638M, and tensile strength, elongation after fracture, and an elastic modulus were evaluated. Moreover, ASTM The Izod impact test was performed according to D256. The obtained result is shown in a table 1.

[0067] (Measurement of the mean-dispersion particle size of nylon 6) After carrying out the golden vacuum evaporation of the fracture surface of the test piece used by the Izod impact test, the layer system of polylactic acid and Nylon 12 was observed using the scanning electron microscope (Akashi factory SIGMA-V), and the mean-dispersion particle size of Nylon 12 was measured. The obtained result is shown in a table 1.

[0068] (Measurement of crystallization time amount) Crystallization time amount was measured with the DSC measuring device (DSC[by PerkinElmer, Inc.]- 7) using the above-mentioned pellet. That is, 0.3mg of samples was paid to the aluminum pan, and time amount after holding for 5 minutes at 200 degrees C, lowering the temperature rapidly, holding and lowering the temperature to 110 degrees C until the endoergic peak of crystallization appears was made into crystallization time amount. The obtained result is shown in a table 1.

[0069] Except having used nylon 6 resin (Ube Industries nylon 1015B) instead of example 2 Nylon 12 resin, like the example 1, resin composite material was produced and measurement of the mean-dispersion particle size of nylon 6 and crystallization time amount was performed in assessment of a distributed condition and kinetic property, and a list. The obtained result is shown in a table 1.

[0070] an example 3 -- the organic-ized montmorillonite was first compounded like the example 1. Next, this organic-ized montmorillonite 3.5g, L-lactide 100g, and octylic acid tin 200mg were put into the reaction container, and it decompressed to 10-2mmHg. Then, temperature was raised gradually, agitating enough and it held at 160 degrees C for 3 hours. furthermore, 2-azacyclo trideca -- non, after introducing 60g in the reaction container and decompressing it again, it held at 180 degrees C for 3 hours, and the target resin composite material was obtained.

[0071] Thus, about the obtained resin composite material, measurement of the mean-dispersion particle size of nylon and crystallization time amount was performed in assessment of a distributed condition and kinetic property, and a list like the example 1. The obtained result is shown in a table 1.

[0072] Without using an example of comparison 1 organic-ized montmorillonite, melting kneading of the same polylactic acid and same Nylon 12 as an example 1 was carried out, and the pellet was produced. About this pellet, measurement of the distributed particle size of Nylon 12 and crystallization time amount was performed in assessment of a distributed condition and kinetic property, and a list like the example 1. The obtained result is shown in a table 2.

[0073] Example 218 of a comparison (OH) Without using, except having performed organic-ization of a montmorillonite only using 12COOH, like the example 1, 2 produced resin composite material and performed measurement of the mean-dispersion particle size of Nylon 12, and crystallization time amount in assessment of a distributed condition and kinetic property, and a list. The obtained result is shown in a table 2.

[0074] Without using, except having performed organic-ization of a montmorillonite only using 18(OH)2, like the example 1, example of comparison 312COOH produced resin composite material, and performed measurement of the mean-dispersion particle size of Nylon 12, and crystallization time amount in assessment of a distributed condition and kinetic property, and a list. The obtained result is shown in a table 2.

[0075] Example 418 of a comparison (OH) Without using, resin composite material was produced except having performed organic-ization of a montmorillonite using stearyl trimethylammonium (C18Me3) like the example 1, and 2 and 12COOH(s) performed

measurement of the mean-dispersion particle size of Nylon 12, and crystallization time amount in assessment of a distributed condition and kinetic property, and a list. The obtained result is shown in a table 2.

[0076]

[A table 1]

	実施例 1	実施例 2	実施例 3
分散状態	○	○	○
引張強さ [MPa]	65.8	78.3	67.9
引張破断伸び [%]	42.5	12.3	51.7
引張弾性率 [GPa]	1.49	1.95	1.55
Izod 衝撃値 [J/m]	58.3	30.3	66.1
ナイロンの 平均分散粒径 [μm]	0.1 以下	0.1 以下	0.1 以下
結晶化時間 [min]	11.2	8.7	10.9

[A table 2]

	比較例 1	比較例 2	比較例 3	比較例 4
分散状態	-	○	○	○
引張強さ [MPa]	20.5	25.0	23.6	39.6
引張破断伸び [%]	1.5	0.8	0.8	1.9
引張弾性率 [GPa]	1.40	1.52	1.51	1.58
Izod 衝撃値 [J/m]	10.3	12.2	10.9	14.5
ナイロンの 平均分散粒径 [μm]	4.3	4.5	4.5	3.8
結晶化時間 [min]	48.5	42.2	41.3	39.8

As shown in a table 1, in the resin composite material of examples 1-3, nylon and polylactic acid were dissolving uniformly enough and minutely, and improvement in toughness, ductility, reinforcement, and an elastic modulus was accepted compared with the melting kneading object (example 1 of a comparison) of polylactic acid and Nylon 12.

[0077] On the other hand, since nylon existed in a polylactic acid matrix as a big particle with a mean-dispersion particle size of several micrometers in the resin composite material of the examples 2-4 of a comparison although the montmorillonite is carrying out detailed distribution into resin as shown in a table 2, sufficient reinforcement effectiveness was not acquired but it only turned out [hard] that it is a weak ingredient.

[0078]

[Effect of the Invention]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] (a) - (c) is the explanatory view showing notionally the condition of the stratified clay mineral made organic by two sorts of organic onium salt, respectively.

[Description of Notations]

1 - A stratified clay mineral, 2a -- Organic onium salt, 2b which have a hydroxyl group -- Organic onium salt which has a carboxyl group.

[Translation done.]

* NOTICES *

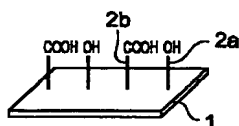
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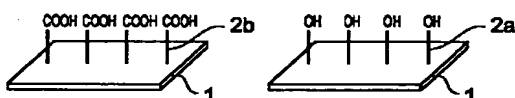
DRAWINGS

[Drawing 1]

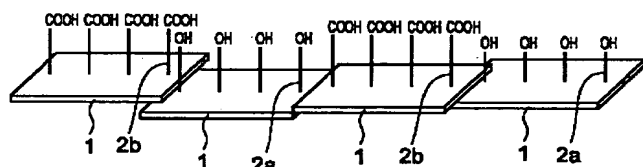
(a)



(b)



(c)



[Translation done.]

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2003-119398

(43)Date of publication of application : 23.04.2003

(51)Int.Cl. C08L101/00
B29B 7/88
C08G 63/91
C08G 69/48
C08K 9/04
C08L 67/00
C08L 77/00

(21)Application number : 2001-312827 (71)Applicant : TOYOTA CENTRAL RES & DEV LAB
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(54) RESIN COMPOSITE MATERIAL AND METHOD FOR PRODUCING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a resin composite material which has excellent dynamic characteristics such as rigidity (strength, elastic modulus and the like), toughness and ductility, and excellent crystallization speed, and comprises at least two polymers and a laminar clay mineral, wherein different kinds of the polymers are sufficiently homogeneously compatibilized between the layers of the laminar clay mineral, and to provide a method for producing the same.

SOLUTION: This resin composite material is characterized by comprising a laminar clay mineral organized with the first and second organic onium salts, the first polymer bound to the laminar clay mineral through the first organic onium salt, and the second polymer bound to the laminar clay mineral through the second organic onium salt.

LEGAL STATUS

[Date of request for examination] 13.04.2004

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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(19)日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11)特許出願公開番号
特開2003-119398
(P2003-119398A)

(43)公開日 平成15年4月23日(2003.4.23)

(51)Int.Cl. ⁷	識別記号	F I	ページコード(参考)
C 0 8 L 101/00	Z B P	C 0 8 L 101/00	Z B P 4 F 2 0 1
B 2 9 B 7/88		B 2 9 B 7/88	4 J 0 0 1
C 0 8 G 63/91		C 0 8 G 63/91	4 J 0 0 2
69/48		69/48	4 J 0 2 9
C 0 8 K 9/04		C 0 8 K 9/04	

審査請求 未請求 請求項の数 8 O L (全 10 頁) 最終頁に続く

(21)出願番号 特願2001-312827(P2001-312827)

(22)出願日 平成13年10月10日(2001.10.10)

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(54)【発明の名称】 樹脂複合材料及びその製造方法

(57)【要約】

【課題】 少なくとも2種のポリマー及び層状粘土鉱物を含有する樹脂複合材料において、層状粘土鉱物の層間に異種のポリマー同士が十分に均一に相溶しており、剛性(強度、弾性率など)、靱性、延性などの力学的特性や結晶化速度に優れた樹脂複合材料、並びにその製造方法を提供すること。

【解決手段】 本発明の樹脂複合材料は、第1及び第2の有機オニウム塩で有機化された層状粘土鉱物と、第1の有機オニウム塩を介して層状粘土鉱物と結合した第1のポリマーと、第2の有機オニウム塩を介して層状粘土鉱物と結合した第2のポリマーとを含有することを特徴とする。

【特許請求の範囲】

【請求項 1】 第 1 及び第 2 の有機オニウム塩で有機化された層状粘土鉱物と、前記第 1 の有機オニウム塩を介して前記層状粘土鉱物と結合した第 1 のポリマーと、前記第 2 の有機オニウム塩を介して前記層状粘土鉱物と結合した第 2 のポリマーとを含有することを特徴とする樹脂複合材料。

【請求項 2】 前記第 1 の有機オニウム塩が水酸基を有する有機オニウム塩であり、前記第 2 の有機オニウム塩がカルボキシル基を有する有機オニウム塩であり、前記第 1 のポリマーが前記第 1 の有機オニウム塩の水酸基を介して前記層状粘土鉱物と結合した脂肪族ポリエステルであり、前記第 2 のポリマーが前記第 2 の有機オニウム塩のカルボキシル基を介して前記層状粘土鉱物と結合した脂肪族ポリアミドであることを特徴とする、請求項 1 に記載の樹脂複合材料。

【請求項 3】 前記第 1 のポリマーがポリ乳酸であることを特徴とする、請求項 1 又は 2 に記載の樹脂複合材料。

【請求項 4】 前記第 1 及び第 2 の有機オニウム塩の炭素数がそれぞれ 6 以上であることを特徴とする、請求項 1～3 のうちのいずれか一項に記載の樹脂複合材料。

【請求項 5】 第 1 及び第 2 の有機オニウム塩で層状粘土鉱物を有機化する有機化工程と、前記有機化工程で得られる層状粘土鉱物と第 1 のポリマーとを熔融混練し、前記第 1 の有機オニウム塩を介して層状粘土鉱物と第 1 のポリマーとを結合させる第 1 の混練工程と、前記有機化工程で得られる層状粘土鉱物と第 2 のポリマーとを熔融混練し、前記第 2 の有機オニウム塩を介して層状粘土鉱物と第 2 のポリマーとを結合させる第 2 の混練工程とを含むことを特徴とする樹脂複合材料の製造方法。

【請求項 6】 水酸基を有する第 1 の有機オニウム塩及びカルボキシル基を有する第 2 の有機オニウム塩で層状粘土鉱物を有機化する有機化工程と、前記有機化工程で得られる層状粘土鉱物と脂肪族ポリエステルとを熔融混練し、前記第 1 の有機オニウム塩の水酸基と前記脂肪族ポリエステル末端カルボキシル基とを反応させる脂肪族ポリエステル混練工程と、前記有機化工程で得られる層状粘土鉱物と脂肪族ポリアミドとを熔融混練し、前記第 2 の有機オニウム塩のカルボキシル基と前記脂肪族ポリポリアミド末端アミノ基とを反応させる脂肪族ポリアミド混練工程とを含むことを特徴とする、請求項 5 に記載の樹脂複合材料の製造方法。

【請求項 7】 第 1 及び第 2 の有機オニウム塩で層状粘土鉱物を有機化する有機化工程と、前記有機化工程で得られる層状粘土鉱物と第 1 の重合性化合物とを混合し、該第 1 の重合性化合物の反応により、前記第 1 の有機オニウム塩を介して前記層状粘土鉱物と結合した第 1 のポリマーを生成させる第 1 の重合工程と、前記有機化工程で得られる層状粘土鉱物と第 2 の重合性化合物とを混合

し、該第 2 の重合性化合物の反応により前記第 2 の有機オニウム塩を介して前記層状粘土鉱物と結合した第 2 のポリマーを生成させる第 2 の重合工程とを含むことを特徴とする樹脂複合材料の製造方法。

【請求項 8】 水酸基を有する第 1 の有機オニウム塩及びカルボキシル基を有する第 2 の有機オニウム塩で層状粘土鉱物を有機化する有機化工程と、前記有機化工程で得られる層状粘土鉱物と α -ヒドロキシ酸の環状二量体及び／又はラクトン類とを混合し、前記第 1 の有機オニウム塩の水酸基を反応点として脂肪族ポリエステルを生成させる脂肪族ポリエステル重合工程と、前記有機化工程で得られる層状粘土鉱物とラクタム類とを混合し、前記第 2 の有機オニウム塩のカルボキシル基を反応点として脂肪族ポリアミドを生成させる脂肪族ポリアミド重合工程とを含むことを特徴とする、請求項 7 に記載の樹脂複合材料の製造方法。

【発明の詳細な説明】**【0001】**

【発明の属する技術分野】 本発明は、樹脂複合材料及びその製造方法に関するものであり、詳しくは、少なくとも 2 種のポリマー及び層状粘土鉱物を含有する樹脂複合材料、並びにその製造方法に関するものである。

【0002】

【従来の技術】 従来、ポリ乳酸などの脂肪族ポリエステルは、微生物や酵素の働きにより分解する性質、いわゆる生分解性を示すことが知られている。そして、脂肪族ポリエステルの生分解速度、あるいは剛性などの力学的特性や結晶化速度といった特性の向上を目的として、有機化剤で有機化された層状粘土鉱物をポリ乳酸に添加した樹脂複合材料が提案されている。

【0003】 例えば特開 2000-17157 号公報、特開 2001-89646 号公報には、脂肪族ポリエステルなどの樹脂と、有機アンモニウム化合物などの有機化剤により有機化された層状粘土鉱物とを含む樹脂組成物が開示されている。

【0004】 また、特開 2000-256087 号公報には、ポリ乳酸などの乳酸系ポリエステルと膨潤性無機フィラーとを含む皮膜材料を用いて肥料の溶出速度を制御した徐放性肥料が開示されており、膨潤性無機フィラーとして、12-アミノドデカン酸アンモニウム塩などで膨潤化された層状ケイ酸塩が例示されている。

【0005】

【発明が解決しようとする課題】 しかしながら、上記従来の樹脂複合材料であっても、剛性、靱性、延性などの力学的特性や結晶化速度の点で必ずしも十分であるとは言えない。そこで、脂肪族ポリエステルの特性を向上させる目的で脂肪族ポリアミドなどを添加する試みがなされているが、脂肪族ポリエステルと脂肪族ポリアミドとは相溶しにくく、これらを十分に均一に分散させることは非常に困難である。

【0006】また、Macromol. Chem. Phys., 199, 2445 (1998)には、 ϵ -カプロラクタムを加水分解した後、これを乳酸と脱水重縮合してポリ乳酸とポリアミドとのブロック共重合体を合成する方法が記載されているが、かかる方法ではオリゴマーが得られるのみであり、実用に供し得る樹脂は未だ得られていない。

【0007】本発明は、上記従来技術の有する課題に鑑みてなされたものであり、少なくとも2種のポリマー及び層状粘土鉱物を含有する樹脂複合材料において、層状粘土鉱物の層間に異種のポリマー同士が十分に均一に相溶しており、剛性（強度、弾性率など）、靱性、延性などの力学的特性や結晶化速度に優れた樹脂複合材料、並びにその製造方法を提供することを目的とする。

【0008】

【課題を解決するための手段】上記課題を解決するために、本発明の樹脂複合材料は、第1及び第2の有機オニウム塩で有機化された層状粘土鉱物と、前記第1の有機オニウム塩を介して前記層状粘土鉱物と結合した第1のポリマーと、前記第2の有機オニウム塩を介して前記層状粘土鉱物と結合した第2のポリマーとを含有することを特徴とする。

【0009】本発明によれば、第1及び第2の有機オニウム塩で層状粘土鉱物を有機化し、この層状粘土鉱物を、第1の有機オニウム塩を介して第1のポリマー、第2の有機オニウム塩を介して第2のポリマーとそれぞれ結合させることによって、これらのポリマー間の相溶性が本来的に低い場合であっても、当該ポリマー同士を層状粘土鉱物の層間において十分に均一に相溶させることができ、その結果、剛性（強度、弾性率など）、靱性、延性などの力学的性質や結晶化速度の点で優れた特性を有する樹脂複合材料が実現される。

【0010】また、本発明の樹脂複合材料の第1の製造方法は、第1及び第2の有機オニウム塩で層状粘土鉱物を有機化する有機化工程と、前記有機化工程で得られる層状粘土鉱物と第1のポリマーとを熔融混練し、前記第1の有機オニウム塩を介して層状粘土鉱物と第1のポリマーとを結合させる第1の混練工程と、前記有機化工程で得られる層状粘土鉱物と第2のポリマーとを熔融混練し、前記第2の有機オニウム塩を介して層状粘土鉱物と第2のポリマーとを結合させる第2の混練工程とを含むことを特徴とするものである。

【0011】また、本発明の樹脂複合材料の第2の製造方法は、第1及び第2の有機オニウム塩で層状粘土鉱物を有機化する有機化工程と、前記有機化工程で得られる層状粘土鉱物と第1の重合性化合物とを混合し、該第1の重合性化合物の反応により、前記第1の有機オニウム塩を介して前記層状粘土鉱物と結合した第1のポリマーを生成させる第1の重合工程と、前記有機化工程で得られる層状粘土鉱物と第2の重合性化合物とを混合し、該第2の重合性化合物の反応により前記第2の有機オニウ

ム塩を介して前記層状粘土鉱物と結合した第2のポリマーを生成させる第2の重合工程と、を含むことを特徴とするものである。

【0012】本発明の第1及び第2の製造方法はいずれも、第1のポリマーと層状粘土鉱物との間に第1の有機オニウム塩を介した結合を形成させると共に、第2のポリマーと層状粘土鉱物との間に第2の有機オニウム塩を介した結合を形成させるもので、これにより層状粘土鉱物の層間において第1のポリマーと第2のポリマーとを十分に均一に相溶させることができるので、力学的特性や結晶化速度に優れた本発明の樹脂複合材料を効率よく且つ確実に得ることができる。

【0013】本発明においては、第1の有機オニウム塩が水酸基を有する有機オニウム塩であり、第2の有機オニウム塩がカルボキシル基を有する有機オニウム塩であり、第1のポリマーが第1の有機オニウム塩の水酸基を介して層状粘土鉱物と結合した脂肪族ポリエステルであり、第2のポリマーが第2の有機オニウム塩のカルボキシル基を介して層状粘土鉱物と結合した脂肪族ポリアミドであることを特徴としてもよい。

【0014】また、本発明の第1の製造方法は、第1及び第2の有機オニウム塩で層状粘土鉱物を有機化する有機化工程と、前記有機化工程で得られる層状粘土鉱物と第1のポリマーとを熔融混練し、前記第1の有機オニウム塩を介して層状粘土鉱物と第1のポリマーとを結合させる第1の混練工程と、前記有機化工程で得られる層状粘土鉱物と第2のポリマーとを熔融混練し、前記第2の有機オニウム塩を介して層状粘土鉱物と第2のポリマーとを結合させる第2の混練工程とを含むことを特徴してもよい。

【0015】また、本発明の第2の製造方法は、水酸基を有する第1の有機オニウム塩及びカルボキシル基を有する第2の有機オニウム塩で層状粘土鉱物を有機化する有機化工程と、前記有機化工程で得られる層状粘土鉱物と α -ヒドロキシ酸の環状二量体及び／又はラクトン類とを混合し、前記第1の有機オニウム塩の水酸基を反応点として脂肪族ポリエステルを生成させる脂肪族ポリエステル重合工程と、前記有機化工程で得られる層状粘土鉱物とラクタム類とを混合し、前記第2の有機オニウム塩のカルボキシル基を反応点として脂肪族ポリアミドを生成させる脂肪族ポリアミド重合工程とを含むことを特徴としてもよい。

【0016】このように水酸基を有する有機オニウム塩とカルボキシル基を有する有機オニウム塩とで有機化された層状粘土鉱物を、水酸基を介して脂肪族ポリエステル、カルボキシル基を介して脂肪族ポリアミドとそれぞれ結合させることによって、本来的に相溶性の低い脂肪族ポリエステルと脂肪族ポリアミドとを層状粘土鉱物の層間で十分に均一に相溶させることができ、剛性、靱性、延性などの力学的特性や結晶化速度に優れた樹脂複

合材料が実現される。なお、当該第1のポリマーがポリ乳酸であると、力学的特性や結晶化速度をさらに向上させることができるので好ましい。

【0017】また、本発明においては、前記第1及び第2の有機オニウム塩の炭素数がそれぞれ6以上であることが好ましい。第1及び第2の有機オニウム塩として炭素数6以上のものを用いると、当該有機オニウム塩により層状粘土鉱物の層間距離が十分に広められるので、第1及び第2のポリマーと層状粘土鉱物との分散均一性が高められ、剛性、靱性、延性などの力学的特性や結晶化速度が向上する傾向にある。

【0018】

【発明の実施の形態】以下、本発明の好適な実施形態について詳細に説明する。

【0019】本発明の樹脂複合材料は、第1及び第2の有機オニウム塩で有機化された層状粘土鉱物と、第1の有機オニウム塩を介して層状粘土鉱物と結合した第1のポリマーと、第2の有機オニウム塩を介して層状粘土鉱物と結合した第2のポリマーとを含有することを特徴とするものである。これにより、第1及び第2のポリマー間の相溶性が本来的に低い場合であっても、当該ポリマー同士を層状粘土鉱物の層間において十分に均一に相溶させることができ、剛性（強度、弾性率など）、靱性、延性などの力学的性質や結晶化速度の点で優れた特性を有する樹脂複合材料が実現される。

【0020】本発明にかかる層状粘土鉱物としては特に制限されないが、具体的には、モンモリロナイト、バイデライト、サポナイト、ヘクトライトなどのスメクタイト族；カオリナイト、ハロサイトなどのカオリナイト族；ジオクタヘドラルパーミキュライト、トリオクタヘドラルパーミキュライトなどのパーミキュライト族；テニオライト、テトラシリシクマイカ、マスコバイト、イライト、セリサイト、フロゴバイト、バイオタイトなどのマイカなどが挙げられる。これらの層状粘土鉱物は、天然鉱物であってもよく、水熱合成、熔融法、固相法などによる合成鉱物であってもよい。また、本発明では、上記の層状粘土鉱物のうちの1種を単独で用いてもよく、2種以上を組み合わせて用いてもよい。また、層状粘土鉱物の陽イオン交換容量は30～300meq/100gであることが好ましい。

【0021】また、本発明において用いられる第1及び第2のポリマーとしては、脂肪族ポリエステル、脂肪族ポリアミド、芳香族ポリアミド、ポリカーボネート、ポリイミド、ポリアルキレンテレフタレート、ポリアリレート、ポリアセタール、ポリフェニレンオキサイド、ポリウレタン、ポリオレフィン等が挙げられるが、脂肪族ポリエステルと脂肪族ポリアミドとを組み合わせて用いると、力学的特性や結晶化速度の点でより優れた樹脂複合材料が実現されるので好ましい。

【0022】また、本発明において用いられる第1及び

第2の有機オニウム塩としては、有機アンモニウム塩、有機ホスホニウム塩、有機ビリジニウム塩、有機スルホニウム塩などのオニウム塩において有機基に水酸基、カルボキシル基、アミノ基、イソシアネート基、エステル基、エポキシ基、酸無水物基等の官能基が結合した化合物が挙げられ、上述したポリマーの種類に応じて当該ポリマーと共有結合を形成可能な官能基を有するものが適宜選定される。例えば、ポリマーとして脂肪族ポリエステル及び脂肪族ポリアミドを用いる場合、水酸基を有する有機オニウム塩を用いることによって当該有機オニウム塩の水酸基を介して脂肪族ポリエステルと層状粘土鉱物を結合させることができ、他方、カルボキシル基を有する有機オニウム塩を用いることによって当該有機オニウム塩のカルボキシル基を介して脂肪族ポリアミドと層状粘土鉱物とを結合させることができる。

【0023】本発明で用いられる第1及び第2の有機オニウム塩の炭素数はそれぞれ6以上であることが好ましい。当該有機オニウム塩の炭素数が6未満であると、層状粘土鉱物の層間距離が十分に広げられず、ポリマーと層状粘土鉱物との分散均一性が低下する傾向にある。

【0024】なお、本発明でいう有機化とは、有機物を層状粘土鉱物の層間及び／又は表面に物理的、化学的方法（好ましくは化学的方法）により吸着及び／又は結合させることを意味し、当該有機オニウム塩による有機化によって層状粘土鉱物の層間距離を十分に広げることができる。また、かかる有機オニウム塩の対アニオンとしては特に制限されないが、例えば Cl^- 、 Br^- 、 I^- などのハロゲンアニオンが好ましく用いられる。

【0025】また、本発明においては、樹脂複合材料に含まれる第1及び第2のポリマーの全てが層状粘土鉱物と結合している必要はなく、それらの一部が結合したものであればよい。

【0026】また、本発明の樹脂複合材料では、上記ポリマーのうちの少なくとも2種と、それらのポリマーと共有結合を形成可能な少なくとも2種の有機オニウム塩とが含有されていればよく、例えば第3の有機オニウム塩及びこれに結合可能な第3のポリマーを更に含有するものであってもよい。

【0027】本発明の特に好ましい実施形態として、第1の有機オニウム塩が水酸基を有する有機オニウム塩であり、第2の有機オニウム塩がカルボキシル基を有する有機オニウム塩であり、第1のポリマーが第1の有機オニウム塩の水酸基を介して層状粘土鉱物と結合した脂肪族ポリエステルであり、第2のポリマーが第2の有機オニウム塩のカルボキシル基を介して層状粘土鉱物と結合した脂肪族ポリアミドである樹脂複合材料を例示することができる。以下、この樹脂複合材料について詳細に説明する。

【0028】水酸基を有する有機オニウム塩の含有量は、層状粘土鉱物100重量部に対して10～150重

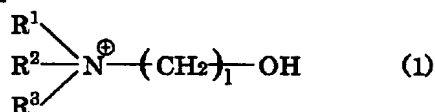
量部であることが好ましく、20～100重量部であることがより好ましい。当該有機オニウム塩の含有量が前記下限値未満であると、層状粘土鉱物の層間距離が十分に広げられず、脂肪族ポリエステル及び脂肪族ポリアミドに対する分散均一性が低下する傾向にあり、他方、前記上限値を超える場合には物理吸着によって導入される有機オニウム塩の量が増加して樹脂複合材料の物性が損なわれる（例えば可塑化）傾向にある。

【0029】本発明で好ましく用いられる水酸基を有する有機オニウム塩としては、水酸基を有するものであれば特に制限されないが、その炭素数は6以上であることが好ましい。当該有機オニウム塩の炭素数が6未満であると、層状粘土鉱物の層間距離が十分に広げられず、脂肪族ポリエステル及び脂肪族ポリアミドに対する分散均一性が低下する傾向にある。水酸基を有し且つ炭素数が6以上である有機オニウム塩としては、下記一般式

(1) 又は (2) で表される有機アンモニウム塩が例示される。これらの有機アンモニウム塩は、1種を単独で用いてもよく、両者を併用してもよい。

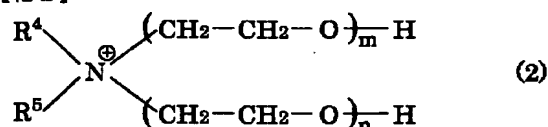
【0030】

【化1】



〔式中、 R^1 、 R^2 及び R^3 は同一でも異なってもよく、それぞれ水素原子又はアルキル基を表し、 l は6～20の整数を表す。〕

【化2】



〔式中、 R^4 及び R^5 は同一でも異なってもよく、それぞれ水素原子又はアルキル基を表し、 R^4 と R^5 との合計の炭素数は6以上であり、 m 及び n は同一でも異なってもよく、1～20の整数を表す。〕

上記一般式(1)中、 R^1 、 R^2 又は R^3 は水素原子又はアルキル基を表す。かかるアルキル基としては、具体的には、メチル基、エチル基、*n*-プロピル基、*i*-プロピル基、*n*-ブチル基、*sec*-ブチル基、*tert*-ブチル基、直鎖又は分岐鎖状のペンチル基、直鎖又は分岐鎖状のヘキシル基、直鎖又は分岐鎖状のオクチル基、直鎖又は分岐鎖状のノニル基、直鎖又は分岐鎖状のデシル基、直鎖又は分岐鎖状のウンデシル基、直鎖又は分岐鎖状のドデシル基、直鎖又は分岐鎖状のトリデシル基、直鎖又は分岐鎖状のテトラデシル基、直鎖又は分岐鎖状のペンタデシル基、直鎖又は分岐鎖状のオクタデシル基などが挙げられ

るが、当該アルキル基の炭素数は1～4であることが好ましい。アルキル基の炭素数が前記上限値を超えると有機オニウム塩の合成が困難となる傾向にある。

【0031】また、上記一般式(1)中、 l はメチレン基($-\text{CH}_2-$)の重合度を表し、6～20、好ましくは8～18の整数である。 l が6未満の場合、層状粘土鉱物の層間距離が十分に広がらず、脂肪族ポリエステル及び脂肪族ポリアミドに対する分散均一性が低下する傾向にある。他方、 l が20を越えると、有機オニウム塩の合成が困難となる傾向にある。

【0032】また、上記一般式(2)中、 R^4 及び R^5 は水素原子又はアルキル基を表す。かかるアルキル基としては、一般式(1)中の R^1 、 R^2 及び R^3 の説明において例示されたアルキル基が挙げられる。

【0033】一般式(2)中の R^4 及び R^5 は同一でも異なってもよいが、それらの合計の炭素数は、6以上であることが好ましく、8以上であることがより好ましい。 R^4 と R^5 との合計の炭素数が6未満であると、層状粘土鉱物の層間距離が十分に広がらず、脂肪族ポリエステル及び脂肪族ポリアミドに対する分散均一性が低下する傾向にある。例えば R^4 が水素原子で R^5 がドデシル基である化合物、 R^4 がメチル基で R^5 がオクタデシル基である化合物、 R^4 及び R^5 がオクタデシル基である化合物は、上記の条件を満たす化合物として好ましく用いられる。

【0034】また、上記一般式(2)中、 m 及び n はオキシエチレン基($-\text{CH}_2\text{CH}_2\text{O}-$)の重合度を表し、1～20、好ましくは1～10、より好ましくは1～5の整数であり、特に好ましくは1である。 m 又は n が20を越えると、層状粘土鉱物の親水性が過剰に高くなり、調整が困難となる傾向にある。なお、 m 及び n は同一でも異なってもよい。

【0035】また、本発明にかかるカルボキシル基を有する有機オニウム塩としては、カルボキシル基を有するものであれば特に制限されないが、その炭素数は6以上であることが好ましい。当該有機オニウム塩の炭素数が6未満であると、層状粘土鉱物の層間距離が十分に広げられず、脂肪族ポリエステル及び脂肪族ポリアミドに対する分散均一性が低下する傾向にある。カルボキシル基を有し且つ炭素数が6以上である有機オニウム塩の好ましい例としては、8-アミノオクチル酸塩酸塩、12-アミノドデカン酸塩酸塩、18-アミノオクタデカン酸塩酸塩などが挙げられる。

【0036】カルボキシル基を有する有機オニウム塩の含有量は、層状粘土鉱物100重量部に対して10～150重量部であることが好ましく、20～100重量部であることがより好ましい。当該有機オニウム塩の含有量が前記下限値未満であると、層状粘土鉱物の層間距離が十分に広げられず、脂肪族ポリエステル及び脂肪族ポリアミドに対する分散均一性が低下する傾向にあり、他

方、前記上限値を超える場合には物理吸着によって導入される有機オニウム塩の量が増加して樹脂複合材料の物性が損なわれる（例えば可塑化）傾向にある。

【0037】また、水酸基を有する有機オニウム塩とカルボキシル基を有する有機オニウム塩との配合比は、樹脂複合材料の特性を損なわない限り特に制限されないが、当該配合比は、水酸基とカルボキシル基とのモル比が好ましくは1:99~99:1、より好ましくは10:90~90:10、さらに好ましくは20:80~80:20の範囲内となるように設定される。水酸基とカルボキシル基とのモル比が前記の範囲外であると、層状粘土鉱物の層間において脂肪族ポリエステルと脂肪族ポリアミドとを均一に相溶させることが困難となる傾向にある。

【0038】図1(a)~(c)はそれぞれ上記2種の有機オニウム塩によって有機化された層状粘土鉱物の状態を概念的に示す説明図である。本発明においては、図1(a)に示すように水酸基を有する有機オニウム塩2aとカルボキシル基を有する有機オニウム塩2bとの双方が層状粘土鉱物1の同一の層に結合していてもよく、図1(b)に示すように2種の有機オニウム塩2a、2bがそれぞれ層状粘土鉱物1の別個の層に結合していてもよく、さらにはこれら2つの結合形態が混在してもよい。また、有機オニウム塩2a、2bが別個の層に結合する場合、図1(c)に示すように層状粘土鉱物1の隣接する各層が端部近傍で連なったフロキュレーション(flocculation)状であると、見かけ上非常に大きいアスペクト比を有する層状粘土鉱物を形成することが可能となるので好ましい。

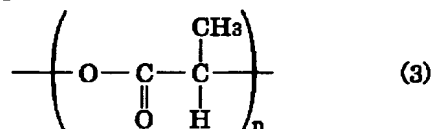
【0039】これらの有機オニウム塩によって層状粘土鉱物の層間距離は十分に広げられ、脂肪族ポリエステル及び脂肪族ポリアミドが層間に導入される。ここで、層状粘土鉱物の層間距離は、各層の重心間の平均距離を基準として5nm以上であることが好ましく、10nm以上であることがより好ましい。層状粘土鉱物の層間距離が前記下限値未満であると、脂肪族ポリエステル及び脂肪族ポリアミドに対する分散均一性が低下する傾向にある。

【0040】また、本発明にかかる脂肪族ポリエステルとしては、例えばグリコリド、ラクチド(Ｌ-ラクチド、Ｄ-ラクチド、meso-ラクチドを含む)などのα-ヒドロキシ酸の環状二量体や、β-プロピオラクトン、ジケテン、γ-ブチロラクトン、δ-バレロラクトン、ε-カプロラクトンなどのラクトン類の開環重合体が挙げられ、当該重合体は単独重合体、共重合体のいずれであってもよい。また、上記重合体の中でもラクチドの開環重合体であるポリ乳酸が好ましい。ポリ乳酸を用いると、剛性、靱性、延性などの力学的特性や結晶化速度が向上する傾向にある。

【0041】本発明において好ましく用いられるポリ乳

酸は、下記一般式(3)：

【化3】



(式中、nは整数を表す)で表される繰り返し単位を有するポリマーである。当該ポリ乳酸の平均分子量は特に制限されないが、5,000~1,000,000であることが好ましい。ポリ乳酸の平均分子量が前記下限値未満であると、強度、弾性率などの機械物性が不十分となる傾向にあり、また、前記上限値を超えると、成形の際に流動性が著しく低下する傾向にある。

【0042】なお、ポリ乳酸の一端には、層状粘土鉱物との間に水酸基を介した結合が形成されるが、他端には、グリコリド、カプロラクトンなどを更に重合させて共重合体としてもよい。かかる共重合体におけるポリ乳酸の重合鎖は、共重合体全体を基準として80mol%以上であることが好ましい。

【0043】また、本発明にかかる脂肪族ポリアミドとしては、ε-カプロラクタム、ラウロラクタム、2-アザシクロオクタノン、2-アザシクロノナノン、2-アザシクロトリデカノンなどのラクタム類の開環重合体(ナイロン)が挙げられ、当該重合体は単独重合体、共重合体のいずれであってもよい。

【0044】脂肪族ポリアミドとの配合量は、脂肪族ポリエステル100重量部に対して1~1000重量部であることが好ましく、10~1000重量部であることがさらに好ましい。脂肪族ポリアミドの配合量が前記下限値未満の場合、樹脂複合材料の耐衝撃性や耐熱性が不十分となる傾向にあり、他方、前記上限値を超えると弾性率が低下する傾向にある。

【0045】また、層状粘土鉱物の配合量は、脂肪族ポリエステルと脂肪族ポリアミドとの配合量の合計100重量部に対して0.01~20重量部であることが好ましく、1~12重量部であることがより好ましい。層状粘土鉱物の配合量が前記下限値未満であると、剛性などの力学的特性や結晶化速度の向上の程度が不十分となる傾向にあり、他方、前記上限値を超える場合には脆化する傾向にある。

【0046】次に、本発明の樹脂複合材料の製造方法について説明する。

【0047】本発明の第1の製造方法は、第1及び第2の有機オニウム塩で層状粘土鉱物を有機化する有機化工程と、有機化工程で得られる層状粘土鉱物と第1のポリマーとを熔融混練し、第1の有機オニウム塩を介して層状粘土鉱物と第1のポリマーとを結合させる第1の混練工程と、有機化工程で得られる層状粘土鉱物と第2のポ

リマーとを熔融混練し、第2の有機オニウム塩を介して層状粘土鉱物と第2のポリマーとを結合させる第2の混練工程とを含むことを特徴とするものである。

【0048】有機化工程は、例えば本出願人により特許第2627194号公報に開示されている方法により行うことができる。すなわち、層状粘土鉱物中の無機イオンを、第1及び第2の有機オニウム塩から生じる有機オニウムイオン（例えば有機アンモニウム塩においては有機アンモニウムイオン）によりイオン交換することによって、層状粘土鉱物の有機化を行うことができる。

【0049】より具体的には、例えば水酸基を有する有機アンモニウム塩とカルボキシル基を有する有機アンモニウム塩とを用いる場合には、次のような方法により有機化を行うことができる。すなわち、塊状の層状粘土鉱物を用いる場合は、先ずこれをボールミルなどにより粉碎し粉体化する。次いで、ミキサーなどを用いてこの粉体を水中に分散させて層状粘土鉱物の水分散物を得る。これとは別に、水酸基を有する有機アミン、カルボキシル基を有する有機アミン及び塩酸などの酸を水に加えて、上記2種類の有機アンモニウム塩を含有する水溶液を調製する。この水溶液を上記層状粘土鉱物の水分散物に加えて混合することにより、層状粘土鉱物中の無機イオンが有機アンモニウム塩から生じた2種類の有機アンモニウムイオンによりイオン交換される。この混合物から水を除去することにより、水酸基を有する有機アンモニウム塩とカルボキシル基を有する有機アンモニウム塩とで有機化された層状粘土鉱物が得られる。

【0050】有機アンモニウム塩や層状粘土鉱物の分散媒体としては、水以外にもメタノール、エタノール、プロパノール、イソプロパノール、エチレングリコール及びこれらの混合物、並びにこれらと水との混合物を使用することができる。

【0051】かかる有機化工程においては、上記したように第1の有機オニウム塩（水酸基を有する有機オニウム塩）及び第2の有機オニウム塩（カルボキシル基を有する有機オニウム塩）による有機化を同時に行ってもよく、一方の有機オニウム塩で有機化した後に他方で有機化してもよい。

【0052】次に、有機化工程で得られる層状粘土鉱物と第1及び第2のポリマーとを熔融混練することによって本発明の樹脂複合材料を得ることができる。例えば、水酸基を有する有機オニウム塩、カルボキシル基を有する有機オニウム塩、脂肪族ポリエステル及び脂肪族ポリアミドを用いる場合、水酸基を有する有機オニウム塩の水酸基と脂肪族ポリエステルの末端カルボキシル基とが反応して両者の間に水酸基を介した結合が形成され、また、カルボキシル基を有する有機オニウム塩のカルボキシル基と脂肪族ポリアミドの末端アミノ基との反応がそれぞれ進行して両者の間にカルボキシル基を介した結合が形成される。これにより、層状粘土鉱物の層間におい

て脂肪族ポリエステルと脂肪族ポリアミドとを十分に均一に相溶させることができ、剛性、靱性、延性などの力学的特性や結晶化速度に優れた本発明の樹脂複合材料を得ることができる。

【0053】なお、第1の製造方法においては、第1のポリマーと層状粘土鉱物との混練と、第2のポリマーと層状粘土鉱物との混練を同時に行ってもよく、これらのポリマーの一方を層状粘土鉱物と混練した後、得られる混練物と他方とを更に混練してもよい（以下、単に「混練工程」というが、当該混練工程は上記した手順の双方を包含するものである）。

【0054】混練工程における温度は、ポリマーと有機オニウム塩との反応の種類に応じて適宜選定される。例えば有機オニウム塩の水酸基と脂肪族ポリエステルの末端カルボキシル基との反応、並びに有機オニウム塩のカルボキシル基と脂肪族ポリアミドの末端アミノ基との反応を行う場合、当該温度の上限値は好ましくは280℃であり、より好ましくは250℃である。当該温度が前記上限値を超えると、脂肪族ポリエステル（あるいは更に脂肪族ポリアミド）の分子量が低下して樹脂複合材料の物性が損なわれる（例えば可塑性）傾向にある。また、当該温度の下限値は脂肪族ポリエステル及び脂肪族ポリアミドの種類によって異なるが、脂肪族ポリエステル又は脂肪族ポリアミドのうち融点が低いポリマーの融点以上であることが好ましい。例えばポリ乳酸の融点は170～180℃であり、ナイロン6の融点は225℃であり、ナイロン12の融点は185℃であるので、これらを組み合わせる場合にはポリ乳酸の融点以上に温度を設定することが好ましい。温度が上記の条件を満たさないと、脂肪族ポリエステルや脂肪族ポリアミドの溶融が不十分となり、これらの分散均一性が低下する傾向にある。

【0055】また、混練工程の際には、本出願人により国際公開WO99/50340号公報に開示されている方法に準じて行うことが好ましい。すなわち、高樹脂換算圧力、高総せん断量、高せん断エネルギーを加えることが可能なスクリュウを備える二軸混練機を用い、樹脂換算圧力の平均値が $5 \times 10^4 \text{ Pa}$ 以上、最大値が $1 \times 10^5 \text{ Pa}$ 、総せん断量が $10^5 \sim 10^7$ 、総せん断エネルギーが $10^{10} \sim 10^{14} \text{ Pa}$ の条件下で有機化された層状粘土鉱物と第1及び第2のポリマーとを熔融混練することによって、これらの分散均一性をより高めることができる。

【0056】本発明の第2の製造方法は、第1及び第2の有機オニウム塩で層状粘土鉱物を有機化する有機化工程と、有機化工程で得られる層状粘土鉱物と第1の重合性化合物とを混合し、該第1の重合性化合物の反応により、第1の有機オニウム塩を介して層状粘土鉱物と結合した第1のポリマーを生成させる第1の重合工程と、有機化工程で得られる層状粘土鉱物と第2の重合性化合物

とを混合し、該第2の重合性化合物の反応により第2の有機オニウム塩を介して前記層状粘土鉱物と結合した第2のポリマーを生成させる第2の重合工程とを含むものである。

【0057】第2の製造方法にかかる有機化工程は、上記第1の製造方法にかかる有機化工程と同様に行うことができる。

【0058】また、第1及び第2の重合工程は同時に行ってもよく、重合工程の一方を行った後に他方を行ってもよい。例えば、脂肪族ポリエステル重合工程及び脂肪族ポリアミド重合工程の順序については以下の(i)～(iii)が例示できる。

(i) 脂肪族ポリエステル重合工程を行った後、脂肪族ポリアミド重合工程を行う；

(ii) 脂肪族ポリアミド重合工程を行った後、脂肪族ポリエステル重合工程を行う；

(iii) 有機化工程で得られる層状粘土鉱物と、 α -ヒドロキシ酸の環状二量体及び／又はラクトン類と、ラクタム類とを混合し、脂肪族ポリエステル重合工程と脂肪族ポリアミド重合工程とを同時に行う。

【0059】上記した手順(i)～(iii)の中でも、手順(i)が特に好ましい。手順(ii)、(iii)では重合の際に生成するアミド(ラクタム又はその開環重合により生成したポリアミド)がラクチド重合の触媒毒となって脂肪族ポリエステルの分子量が不十分となる恐れがあるが、手順(i)によればこのような現象を十分に抑制することができ、分子量が十分に大きい脂肪族ポリエステルを生成させることができる。

【0060】また、上記脂肪族ポリエステル重合工程及び脂肪族ポリアミド重合工程は、所定の触媒を用いて行ってもよく、無触媒で行ってもよい。触媒としては、具体的には、オクチル酸化スズ、塩化スズ、塩化亜鉛、酸化鉛、炭酸鉛、塩化チタン、アルコキシチタン、酸化ゲルマニウム、酸化ジルコニウムなどが挙げられ、その使用量は重合性単量体100重量部に対して0.001～1重量部であることが好ましい。また、当該重合工程における反応温度は100～200℃であることが好ましい。

【0061】このように本発明の第1及び第2の製造方法はいずれも、第1のポリマーと層状粘土鉱物との間に第1の有機オニウム塩を介した結合を形成させると共に、第2のポリマーと層状粘土鉱物との間に第2の有機オニウム塩を介した結合を形成させるもので、これにより層状粘土鉱物の層間において第1のポリマーと第2のポリマーとを十分に均一に相溶させることができるので、力学的特性や結晶化速度に優れた本発明の樹脂複合材料を効率よく且つ確実に得ることができる。

【0062】

【実施例】以下、実施例及び比較例に基づいて本発明を更に具体的に説明するが、本発明は以下の実施例に何ら

限定されるものではない。

【0063】実施例1

(層状粘土鉱物の有機化) ナトリウム型モンモリロナイト(クニミネ鉱業製クニピアF、陽イオン交換容量：115meq/100g)100gを80℃の水5000mlに分散させ、一方、ジヒドロキシエチルメチルステアрилアンモニウムブロミド(以下、18(OH)₂という)36.4g、12-アミノドデカン酸(以下、12COOHという)7.4g及び濃塩酸3.3mlを80℃の水2000mlに溶解させた。次いで、両者を混合してモンモリロナイトの有機化を行い18(OH)₂と12COOHとが7：3のモル比で付加した有機化モンモリロナイトを得た。得られた有機化モンモリロナイト(以下、18(OH)₂-Montという)を80℃の水で3回洗浄し、凍結乾燥した後、これを粉碎した。灼残法により求めた有機化モンモリロナイトの無機分の残量は64%であった。

【0064】(ポリ乳酸及びナイロン12の混練) スクリューを備える二軸押出機(日本製鋼所製TEX30 α)を用い、ポリ乳酸樹脂(島津製作所製ラクティ#9030)に上記の有機化モンモリロナイトを無機分換算値で4.3重量%添加した混合物を、スクリュー回転数300rpm、樹脂温度200℃、樹脂供給速度5kg/hで熔融混練した。この混練の途中から、ナイロン12樹脂(宇部興産製ナイロン3024B)を、ポリ乳酸とナイロン12との重量比が7：3となるようにして添加し、更に熔融混練を行って目的の樹脂複合材料を得た。得られた樹脂複合材料をストランド状に押し出した後、水で急冷し、ストランドカッターでペレットとした。

【0065】(分散状態の評価) 上記のペレットをミクロトームで切り出して超薄切片を作製した。これを透過型電子顕微鏡(日本電子製JOLE-200CX)で観察し、層状粘土鉱物の分散状態を以下の基準：

○：層状粘土鉱物がほぼ単層ごとに微分散している

△：2～3層が凝集した状態の層状粘土鉱物が50%以上認められる

×：ほとんどの層状粘土鉱物が数十層以上凝集した状態で分散している

に基づいて評価した。得られた結果を表1に示す。

【0066】(力学的特性の評価) 射出成形機(日精樹脂工業製PS40E2ASE)及びFS75型を用いて上記の樹脂複合材料の射出成形を行い、ダンベル型引張試験片を得た。この試験片を用い、ASTM D638Mに準じて引張り試験を行い、引張強さ、破断伸び、弾性率を評価した。また、ASTM D256に準じてIzod衝撃試験を行った。得られた結果を表1に示す。

【0067】(ナイロン6の平均分散粒径の測定) Izod衝撃試験で用いた試験片の破断面を金蒸着した後、走査型電子顕微鏡(明石製作所製SIGMA-V)を用

いてポリ乳酸とナイロン12の層構造を観察し、ナイロン12の平均分散粒径を測定した。得られた結果を表1に示す。

【0068】（結晶化時間の測定）上記のペレットを用い、DSC測定装置（パーキンエルマー社製DSC-7）により結晶化時間を測定した。すなわち、試料0.3mgをアルミパンに入れ、200℃で5分間保持してから110℃まで急激に降温して保持し、降温してから結晶化の吸熱ピークが現れるまでの時間を結晶化時間とした。得られた結果を表1に示す。

【0069】実施例2

ナイロン12樹脂の代わりにナイロン6樹脂（宇部興産製ナイロン1015B）を用いたこと以外は実施例1と同様にして、樹脂複合材料を作製し、分散状態及び力学的特性の評価、並びにナイロン6の平均分散粒径及び結晶化時間の測定を行った。得られた結果を表1に示す。

【0070】実施例3

まず、実施例1と同様にして有機化モンモリロナイトを合成した。次に、この有機化モンモリロナイト3.5g、L-ラクチド100g、オクチル酸スズ200mgを反応容器に入れ、10⁻²mmHgまで減圧した。続いて十分攪拌しながら徐々に温度を上昇させ、160℃で3時間保持した。更に、2-アザシクロトリデカノン60gを反応容器内に導入し、再度減圧した後180℃で3時間保持して目的の樹脂複合材料を得た。

【0071】このようにして得られた樹脂複合材料について、実施例1と同様にして分散状態及び力学的特性の評価、並びにナイロンの平均分散粒径及び結晶化時間の測定を行った。得られた結果を表1に示す。

【0072】比較例1

有機化モンモリロナイトを用いず、実施例1と同様のポリ乳酸及びナイロン12を熔融混練してペレットを作製した。このペレットについて、実施例1と同様にして分散状態及び力学的特性の評価、並びにナイロン12の

分散粒径及び結晶化時間の測定を行った。得られた結果を表2に示す。

【0073】比較例2

18(OH)₂は用いず、12COOHのみを用いてモンモリロナイトの有機化を行ったこと以外は実施例1と同様にして、樹脂複合材料を作製し、分散状態及び力学的特性の評価、並びにナイロン12の平均分散粒径及び結晶化時間の測定を行った。得られた結果を表2に示す。

【0074】比較例3

12COOHは用いず、18(OH)₂のみを用いてモンモリロナイトの有機化を行ったこと以外は実施例1と同様にして、樹脂複合材料を作製し、分散状態及び力学的特性の評価、並びにナイロン12の平均分散粒径及び結晶化時間の測定を行った。得られた結果を表2に示す。

【0075】比較例4

18(OH)₂及び12COOHは用いず、ステアリルトリメチルアンモニウム(C₁₈Me₃)を用いてモンモリロナイトの有機化を行ったこと以外が実施例1と同様にして、樹脂複合材料を作製し、分散状態及び力学的特性の評価、並びにナイロン12の平均分散粒径及び結晶化時間の測定を行った。得られた結果を表2に示す。

【0076】

【表1】

	実施例1	実施例2	実施例3
分散状態	○	○	○
引張強さ[MPa]	65.8	78.3	67.9
引張破断伸び[%]	42.5	12.3	51.7
引張弾性率[GPa]	1.49	1.95	1.55
Izod衝撃値[J/m]	58.3	30.3	66.1
ナイロンの平均分散粒径[μm]	0.1以下	0.1以下	0.1以下
結晶化時間[min]	11.2	8.7	10.9

【表2】

	比較例1	比較例2	比較例3	比較例4
分散状態	-	○	○	○
引張強さ[MPa]	20.6	25.0	23.6	39.6
引張破断伸び[%]	1.5	0.8	0.8	1.9
引張弾性率[GPa]	1.40	1.52	1.51	1.58
Izod衝撃値[J/m]	10.3	12.2	10.9	14.5
ナイロンの平均分散粒径[μm]	4.3	4.6	4.5	3.8
結晶化時間[min]	48.5	42.2	41.3	39.8

表1に示したように、実施例1～3の樹脂複合材料においては、ナイロンとポリ乳酸とが十分に均一に且つ微細に相溶しており、ポリ乳酸とナイロン12との熔融混練物（比較例1）に比べて靱性、延性、強度及び弾性率の向上が認められた。

【0077】これに対して、表2に示したように、比較例2～4の樹脂複合材料においては、樹脂中にモンモリロナイトが微細分散しているものの、ナイロンが平均分散粒径数μmの大きな粒子としてポリ乳酸マトリックス

中に存在するため、十分な補強効果が得られておらず、単に硬く脆い材料であることがわかった。

【0078】

【発明の効果】以上説明した通り、本発明によれば、第1及び第2の有機オニウム塩で層状粘土鉱物を有機化し、この層状粘土鉱物を、第1の有機オニウム塩を介して第1のポリマー、第2の有機オニウム塩を介して第2のポリマーとそれぞれ結合させることによって、これらのポリマー間の相溶性が本来的に低い場合であっても、

当該ポリマー同士を層状粘土鉱物の層間において十分に均一に相溶させることができ、その結果、剛性（強度、弾性率など）、靱性、延性などの力学的性質や結晶化速度の点で優れた特性を有する樹脂複合材料が実現される。

【0079】また、本発明の樹脂複合材料の製造方法によれば、このように優れた特性を有する本発明の樹脂複合材料を効率よく且つ確実に得ることができる。

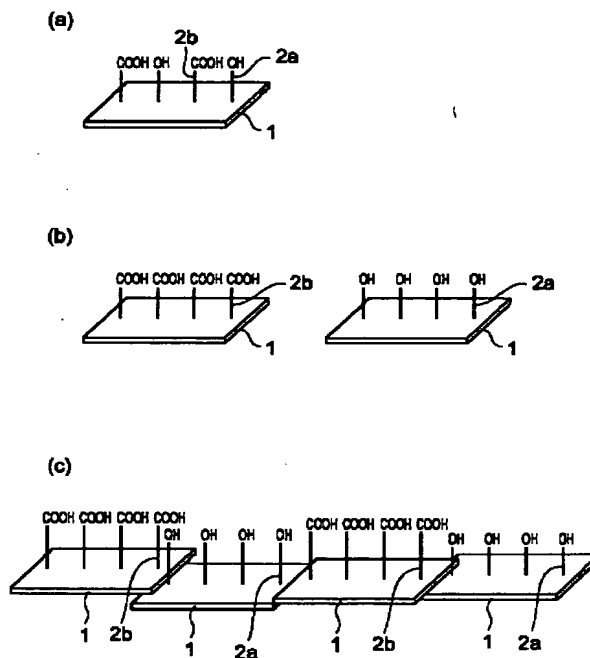
【図面の簡単な説明】

【図1】（a）～（c）はそれぞれ2種の有機オニウム塩によって有機化された層状粘土鉱物の状態を概念的に示す説明図である。

【符号の説明】

1…層状粘土鉱物、2a…水酸基を有する有機オニウム塩、2b…カルボキシル基を有する有機オニウム塩。

【図1】



フロントページの続き

(51) Int. Cl. 7

C 08 L 67/00
77/00

識別記号

F I

C 08 L 67/00
77/00

ターマコード（参考）

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Fターム（参考） 4F201 AA24K AA29K AB11 AB16

AB19 AB24 AB28 AD20 AD27
BA01 BC37 BD05 BK02 BK12
BN44

4J001 DA01 DD13 EA02 EA06 EA08
GA01 GE02 GE04 GE05 GE06
JB21

4J002 CF18W CL01X DJ006 FB086

4J029 AA02 AB07 AE01 EA05 JA283

JB063 JC093 JC383 JC633

KH01